

Silaacetylene: A Possible Target for Experimental Studies

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ABSTRACT

The equilibrium geometries and transition states for interconversion of the CSiH_2 isomers in the singlet electronic ground state are optimized at the MP2 and CCSD(T) levels of theory using a TZ2P basis set. The heats of formation, vibrational frequencies, infrared intensities, and rotational constants are also predicted. There are three energy minima on the CSiH_2 potential energy surface. Energy calculations at CCSD(T)/TZ2P(fd) + ZPE predict that the global energy minimum is silavinylidene (**1**), which is $34.1 \text{ kcal mol}^{-1}$ lower in energy than trans-bent silaacetylene (**2**) and $84.1 \text{ kcal mol}^{-1}$ more stable than the vinylidene isomer (**3**). The barrier for rearrangement $2 \rightarrow 1$ is calculated at the same level of theory to be $5.1 \text{ kcal mol}^{-1}$, while for the rearrangement $3 \rightarrow 2$ a barrier of $2.7 \text{ kcal mol}^{-1}$ is predicted. The natural bond orbital (NBO) population scheme indicates a clear polarization of the C—Si bonds toward the carbon end. A significant ionic contribution to the C—Si bonds of **1** and **2** is suggested by the NBO analysis. The C—Si bond length of trans-bent silaacetylene (**2**) is longer than previously calculated [1.665 \AA at CCSD(T)/TZ2P]. The calculated carbon–silicon bond length of **2** is in the middle between the C—Si double bond length of **1** (1.721 \AA) and the C—Si triple bond of the linear form HCSiH (**4**), which is 1.604 \AA . Structure **4** is a higher-order saddle point on the potential energy surface. © 1996 by John Wiley & Sons, Inc.

Introduction

The chemistry of the silicon analogues of ethylene and acetylene is a fascinating example of the interplay of theoretical and experimental research.¹ In particular, the story of the theoretical

predictions² and experimental observations³ of Si_2H_2 isomers is striking proof for the strength of combining modern quantum mechanical methods with sophisticated experimental techniques. Linear disilaacetylene is not a minimum on the Si_2H_2 potential energy surface.² The trans-bent structure of Si_2H_2 is $20.5 \text{ kcal mol}^{-1}$ lower in energy (CI/TZ2P + ZPE) than the linear form.^{2d} The global energy minimum on the Si_2H_2 potential

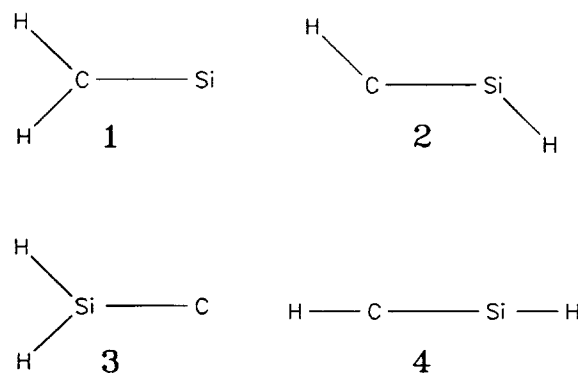
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energy surface has an unusual doubly bridged butterfly structure, which is $22.6 \text{ kcal mol}^{-1}$ more stable (CI/TZ2P + ZPE) than the trans-bent form.^{2d}

There is less information available about monosilicon analogues of acetylene. On the theoretical side, most of the stationary points on the CSiH_2 potential energy surface have been optimized only at the Hartree-Fock (HF) level of theory.⁴⁻⁷ Three energy minimum forms have been found. The global energy minimum structure is the silylidene isomer (1). The trans-bent form of silaacetylene (2) is calculated to be approximately 40 kcal mol^{-1} higher in energy at either MP3/6-31G(d)⁴ or CI/DZP.⁵ A remarkable feature of the latter isomer is that it is not a stationary point at the HF level of theory.⁴ A barrier for rearrangement of 2 to 1 is predicted only at correlated levels of theory.⁴ This is unusual, because electron correlation typically lowers or entirely eliminates barriers predicted at the self-consistent field (SCF) level. Calculations at MP3/6-31G(d)⁴ and CI/DZP⁵ predict that the activation energy for rearrangement $2 \rightarrow 1$ is approximately $5\text{--}9 \text{ kcal mol}^{-1}$. The third CSiH_2 isomer is the vinylidene species 3. This isomer is predicted to be ca. 90 kcal mol^{-1} higher in energy than 1.⁵ The linear form 4 is not a minimum on the potential energy surface.⁴⁻⁷

There is only one experimental study which gives evidence for the formation of a CSiH_2 species. Recently, Srinivas, Sülzle, and Schwarz⁸ reported the results of neutralization-reionization mass spectrometric experiments (NRMS)⁹ using $\text{H}_3\text{SiCH}_2\text{Cl}$ as a precursor. The recovery signal at m/z 42 and the fragmentation pattern strongly suggest that the observed compound has the connectivity SiCH_2 (1).⁸ It appears that the global energy minimum structure on the CSiH_2 potential energy surface 1 has experimentally been observed. The question remains if the silaacetylene isomer 2 can also be detected by experimental techniques. After the successful preparation and identification of molecules containing a carbon-silicon double bond,^{1,10} this would be the first compound which contains a (formal) carbon-silicon triple bond. It would be helpful for such studies if theory would provide accurate information about the structures, energies, and properties of the CSiH_2 isomers. In a recent review about theoretical aspects of organosilicon compounds, it was concluded that "it is highly desirable to study these molecule with the presently available more accurate theoretical methods."^{1a}

This article presents the results of an extensive



SCHEME 1. CSiH_2 structures investigated in this study.

study of the CSiH_2 potential energy surface in the electronic singlet state on a high level of theory. Triplet states have not been considered, because previous studies have shown that they are clearly higher in energy than the singlet states.^{6,7} We give the optimized geometries, energies, and vibrational frequencies of the CSiH_2 energy minimum structures 1, 2, and 3 and the transition states for rearrangement $2 \rightarrow 1$ and $3 \rightarrow 2$ at the CCSD(T) level of theory using large basis sets of TZ2P quality. We also present the rotational constants of 1-3 in order to facilitate the analysis of experimental rotational spectra. The heat of formation at 0 K ΔH_f° of the CSiH_2 isomers is predicted by calculating the heats of hydrogenation. The bonding in the CSiH_2 isomers is discussed based on the analysis of the electronic structure using the NBO method.¹¹

Methods

Because previous studies have shown^{4,5} that the Hartree-Fock level of theory is insufficient for even a qualitative description of the CSiH_2 potential energy surface, we employed correlated wave functions from the start in this research. Geometry optimizations at the HF level have only been carried out for 1, 3, and 4 for comparative reasons. The geometries of the stationary points were first optimized using Møller-Plesset perturbation theory terminated at second order (MP2).¹² The MP2 optimized structures have then been used as starting points for geometry optimizations at the CCSD(T) level of theory (coupled-cluster method with single and double excitations and perturbative estimates of the triple excitations).¹³ Stationary points were located precisely using analytical gradient methods. The characterization of the station-

ary points were performed by evaluating the nuclear Hessian via analytical (MP2)¹⁴ or numerical [CCSD(T)] second derivatives. The harmonic vibrational frequencies, infrared intensities, and zero-point vibrational energies (ZPE) have been calculated at MP2 and CCSD(T). The theoretical frequencies and ZPE values are unscaled.

The basis set for silicon is a 6s5p contraction¹⁵ of Huzinaga's 12s9p primitive set,¹⁶ augmented by two sets of spherical *d*-type polarization functions with exponents $\alpha_d = 0.23$ and 0.69. The basis sets for carbon and hydrogen are triple-zeta contractions¹⁷ of Huzinaga's primitive Gaussian sets¹⁶ (9s5p/5s3p) and (5s/3s) augmented by two sets of *d* functions for carbon (exponents $\alpha_d = 0.46$ and 1.39) and two sets of *p* functions for hydrogen (exponents $\alpha_p = 0.46$ and 1.39), respectively. This basis set is noted as TZ2P. Geometry optimizations have been carried out at the MP2/TZ2P and CCSD(T)/TZ2P levels of theory. Improved energies have been calculated for the CCSD(T)/TZ2P optimized stationary points on the potential energy surface at the CCSD(T) level using the TZ2P basis set extended by one additional set of *f* polarization functions for silicon ($\alpha_f = 0.32$) and carbon ($\alpha_f = 0.80$) and a set of *d* functions for hydrogen ($\alpha_d = 1.00$). This basis set is denoted as TZ2P(fd). Unless otherwise noted, the energies discussed in this article refer to calculations at CCSD(T)/TZ2P(fd)//CCSD(T)/TZ2P. All electrons have been correlated in the MP2 and CCSD(T) calculations.

The calculations have been carried out using the programs ACESII¹⁸ and Gaussian 92.¹⁹ The NBO analysis¹² was carried out with the subroutine available in Gaussian 92.¹⁹

Results and Discussion

Table I shows the energies of the CSiH₂ isomers. Figure 1 displays the optimized geometries of the stationary points on the CSiH₂ potential energy surface. Figure 2 shows the energy profile of the CSiH₂ potential energy surface in the singlet ground state calculated at CCSD(T)/TZ2P(fd)//CCSD(T)/TZ2P.

The global energy minimum structure 1 is predicted with a carbon-silicon bond length of 1.721 Å at the CCSD(T)/TZ2P level of theory (Fig. 1). This is clearly longer than the C—Si distance calculated at HF/TZ2P (1.696 Å). A previous calculation of silylidene (1) at the HF level using a DZ + *d* basis set gave a C—Si bond length of 1.698 Å,

TABLE I. Calculated Total Energies E (au), Relative Energies E_{rel} (kcal mol⁻¹), Zero-Point Vibrational Energies ZPE (kcal mol⁻¹), and Number of Imaginary Frequencies i .

Molecule	No.	Sym.	HF / TZ2P			MP2 / TZ2P			CCSD(T) / TZ2P			CCSD(T) / TZ2P(fd)		
			E_{tot}	E_{rel}	i	E_{tot}	E_{rel}	ZPE	E_{tot}	E_{rel}	ZPE	E_{tot}	E_{rel}	i
H ₂ CSi	1	C _{2v}	-327.89296	0.0	0	-328.28101	0.0	13.7	-328.32170	0.0	13.7	-328.34746	0.0	0
HCSiH	2	C _s	-327.76204	82.2	0	-328.22094	37.7	12.7	-328.26427	36.0	12.0	-328.29046	35.8	0
CSiH ₂	3	C _{2v}	-327.80372	56.0	0	-328.12734	96.4	10.9	-328.18164	87.9	9.8	-328.20719	88.0	0
HCSiH	4	C _{∞v}			2	-328.21560	41.0	11.8	-328.24990	45.1	11.7	-328.27736	44.0	2
TS1		C _s			1	-328.19965	51.1	11.6	-328.25466	42.1	11.1	-328.28092	41.8	1
TS2		C _s			1	-328.12288	99.2	9.3	-328.17567	91.6	8.7	-328.20134	91.7	2
TS2		C ₁							-328.17568	91.6	8.8	-328.20131	91.7	1
SiH ₄		T _d							-291.55080		20.0	-291.56771		0
CH ₄		T _d							-40.44074		28.3	-40.45776		0
H ₂		D _{∞h}							-1.17073		6.3	-1.17220		0

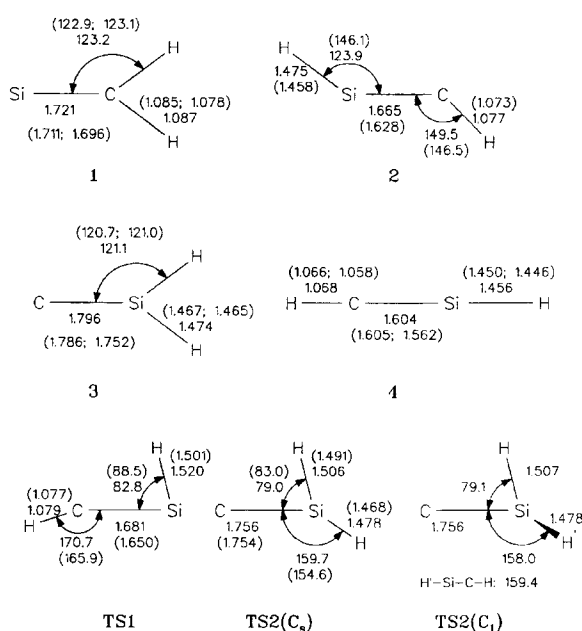


FIGURE 1. Optimized geometries at CCSD(T)/TZ2P. Values at MP2/TZ2P followed by HF/TZ2P data are given in parentheses.

which is very similar to the value at HF/TZ2P.⁵ This indicates that further improvement of the basis set beyond TZ2P should not have a significant influence on the predicted C—Si interatomic distance. The MP2 value for the C—Si bond length

of **1** (1.711 Å) is longer than the HF value. Figure 1 shows that inclusion of higher excitations at CCSD(T) yields an even longer C—Si bond than at MP2. Previous theoretical studies indicate that the bond lengths of multiple bonds are predicted to be slightly (< 0.01 Å) too long at CCSD(T)/TZ2P.²⁰ This means that the correct C—Si bond length of **1** should be 1.71–1.72 Å, which is a little longer than the bond length of a standard carbon–silicon double bond (1.69 Å).^{1c,1d}

A focus of the present study is the structure and potential well depth of the next higher-lying isomer silaacetylene (**2**). Structure **2** is not a minimum on the potential energy surface at the HF level.^{4,5} The only previous study which reports the optimized geometry of **2** at a correlated level was carried out by Hoffmann, Yoshioka, and Schaefer (HYS).⁵ These workers reported a C—Si bond length of 1.635 Å for the trans-bent form of silaacetylene obtained at CI/DZ + d.⁵ Figure 1 shows that the C—Si bond at CCSD(T)/TZ2P is 1.665 Å, which is somewhat longer than the value reported by HYS. The MP2/TZ2P value for the C—Si bond distance (1.628 Å) is close to the CI/DZ + d value and significantly shorter than the CCSD(T)/TZ2P result. Under consideration of the accuracy of the CCSD(T)/TZ2P level,²⁰ we think that the true bond length of **2** is 1.65–1.66 Å. This is clearly shorter than the carbon–silicon bond length of **1**, but longer than the bond length calcu-

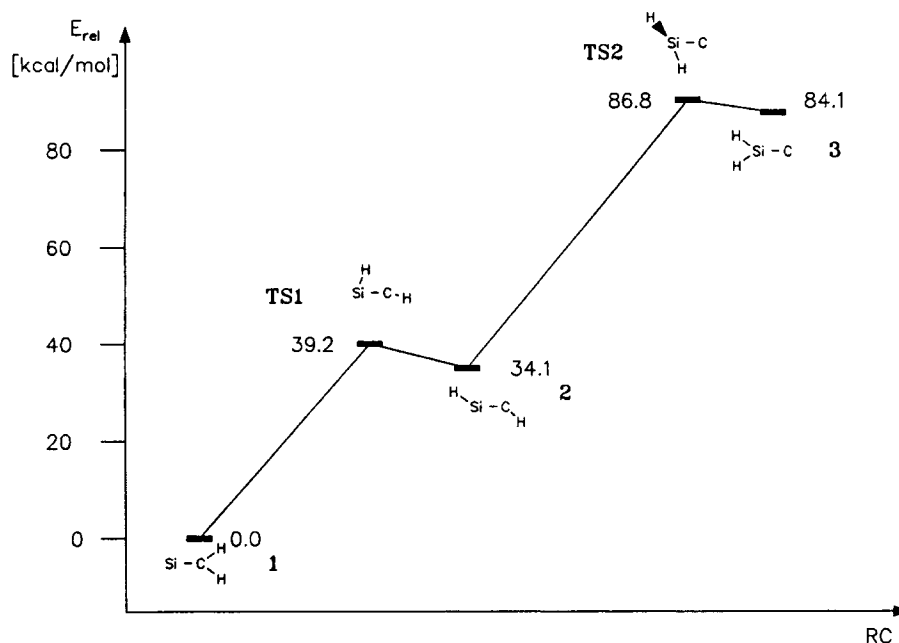


FIGURE 2. Calculated reaction profile for the rearrangement of singlet CSiH_2 . Energy values at CCSD(T)/TZ2P(fd) + ZPE using CCSD(T)/TZ2P optimized geometries.

lated at CCSD(T)/TZ2P for the linear form **4** (1.604 Å). If the latter value is taken as reference for a carbon–silicon triple bond length, the interatomic distance predicted for **2** is in the middle between a C—Si triple and double bond. Noteworthy is the C—Si—H bond angle, which is calculated to be much smaller at CCSD(T) (123.9°) than at the MP2 level (146.1°). A previous CI/DZ + d optimization of **2** gave a C—Si—H bond angle 128.8°. ⁵

Trans-bent silaacetylene (**2**) is calculated at CCSD(T)/TZ2P(fd) to be 35.8 kcal mol⁻¹ higher in energy than silylidene (**1**). The energy difference is reduced to 34.1 kcal mol⁻¹ with inclusion of ZPE corrections. An attempt was made to locate a cis-bent form of silaacetylene on the potential energy surface. Starting from reasonable cis structures, several optimizations at the MP2/TZ2P and CCSD(T)/TZ2P levels proved fruitless. The total energy was always above that of the constrained linear form **4**, which is a higher-order saddle point (*i* = 2) at the MP2/TZ2P and CCSD(T)/TZ2P levels of theory. The calculations indicate that there is no cis-bent isomeric form of silaacetylene.

We optimized the transition state **TS1** for 1,2-hydrogen migration **2** → **1** at MP2/TZ2P and CCSD(T)/TZ2P. The optimized structure of **TS1** is shown in Figure 1. **TS1** has a planar geometry. The migrating hydrogen atom is bridging the carbon and silicon atoms, but the Si—H bond is only slightly elongated in the transition state. The geometry of **TS1** is closer to **2** than to **1**, which is in agreement with the Hammond postulate.²¹ The calculated well depth at MP2/TZ2P is 13.4 kcal mol⁻¹, which becomes 12.3 kcal mol⁻¹ when ZPE effects are included (Table I). A significantly lower barrier of 6.0 kcal mol⁻¹ is predicted at the more accurate CCSD(T)/TZ2P(fd) level. The activation energy **2** → **1** becomes 5.1 kcal mol⁻¹ at CCSD(T)/TZ2P(fd) + ZPE. We think that this is a sufficiently high barrier to make it possible to observe and identify the trans-bent silaacetylene isomer **2** under appropriate experimental conditions. Our confidence is based on the success of the theoretical and experimental studies of Si₂H₂ isomers. The monobridged structure of Si₂H₂ was predicted at the CCSD(T)/TZ2df + ZPE level of theory (TZ2p at hydrogen) to lie 8.7 kcal mol⁻¹ above the dibridged global energy minimum form.^{2b} The barrier for rearrangement was calculated to be only 3.7 kcal mol⁻¹.^{2b} In spite of the low activation barrier, the higher-lying monobridged isomer of Si₂H₂ has been observed in a low-pressure silane plasma.^{3b} Attempts to observe silaacetylene **2** might also be successful.

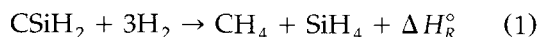
The third CSiH₂ isomer investigated by us is the vinylidene species **3**. Figure 1 shows the optimized geometry of **3** at HF, MP2, and CCSD(T) using the TZ2P basis set. Structure **3** has previously been calculated at the HF level.^{5,6} The C—Si bond length of **3** was calculated to be 1.752 Å at HF/DZ + d.⁵ The same value is predicted at HF/TZ2P (Fig. 1). The carbon–silicon bond length becomes longer at the correlated level. At CCSD(T)/TZ2P, the C—Si interatomic distance becomes 1.796 Å, which is significantly longer than the C—Si bond length of **1** (1.721 Å). The isomeric form **3** is thermodynamically rather unstable. Structure **3** is 84.1 kcal mol⁻¹ higher in energy than **1** and 50.0 kcal mol⁻¹ higher in energy than **2** at CCSD(T)/TZ2P + ZPE (Table I).

The vinylidene isomer **3** is a very shallow minimum on the CSiH₂ potential energy surface. The transition state for hydrogen migration **3** → **2** (**TS2**) is calculated to be only 2.7 kcal mol⁻¹ higher in energy than **3** at CCSD(T)/TZ2P(fd) + ZPE. The energy barrier is 1.2 kcal mol⁻¹ at MP2/TZ2P + ZPE. The optimized structure of **TS2** at MP2/TZ2P has C_s symmetry (Fig. 1). An attempt to optimize **TS2** with the constraint of planarity at CCSD(T)/TZ2P led to a structure with two imaginary frequencies. The optimization without symmetry constraint gave the nonplanar transition state **TS2** shown in Figure 1. Previous calculations at the HF level indicated also that **TS2** might have a nonplanar geometry, but the geometry optimization was not possible for technical reasons.⁵ However, the nonplanar structure **TS2**(C₁) is 0.02 kcal mol⁻¹ higher in energy than the planar form **TS2**(C_s) at CCSD(T)/TZ2P(df) (Table I). Because of the very high energy of **3** relative to **1**, and because the activation barrier for rearrangement **3** → **2** is rather low, it will be very difficult to observe the vinylidene isomer **3** experimentally.

We tried to locate other local minima on the CSiH₂ potential energy surface in the electronic state. The search was inspired by the theoretically predicted large number of Si₂H₂ energy minima, which have very unusual structures.² All attempts to find energy minimum structures other than **1**, **2**, and **3** using different starting geometries were fruitless.[†] The structures shown in Figure 1 are probably the only isomeric forms of CSiH₂ which are minima on the potential energy surface in the singlet ground state.

[†]We did not look for possible van der Waals complexes between H₂ and CSi, which might exist as weakly bound adducts.

We calculated the heats of formation ΔH_f° at 0 K of 1–3 using the theoretically predicted heats of hydrogenation (reaction 1):



The reaction enthalpy of eq. (1) calculated for 1 at CCSD(T)/TZ2P(fd) using CCSD(T)/TZ2P optimized geometries is $-85.6 \text{ kcal mol}^{-1}$.[‡] This value together with the experimentally observed²² values $\Delta H_f^\circ(\text{CH}_4) = -16.0 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{SiH}_4) = 11 \text{ kcal mol}^{-1}$ gives a theoretically predicted heat of formation $\Delta H_f^\circ(1) = 80.6 \text{ kcal mol}^{-1}$. The heats of formation of the other CSiH₂ isomers calculated at the same level of theory are $\Delta H_f^\circ(2) = 114.7 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(3) = 164.7 \text{ kcal mol}^{-1}$.

Table II shows the calculated harmonic vibrational frequencies, infrared (IR) intensities, rotational constants, and dipole moments at CCSD(T)/TZ2P. The C—Si stretching mode of 1 is predicted to have a frequency of 925 cm^{-1} . The silaacetylene isomer 2 is calculated with a higher frequency (1059.4 cm^{-1}) for the carbon-silicon fundamental. This is in agreement with the calculated shorter C—Si bond length of 2 than those of 1. Previous theoretical studies indicate that calcu-

[‡]The energies of H₂, SiH₄, and CH₄ are given in Table I. The optimized bond lengths at CCSD(T)/TZ2P are H—H: 0.742 \AA ; Si—H: 1.477 \AA ; C—H: 1.087 \AA .

lated harmonic vibrational frequencies for the stretching modes of A—B multiple bonds of HCN, HNC, HCCH, H₂CO, and FCCH at CCSD(T)/TZ2P are very close to experimental anharmonic frequencies.²⁰ The experimental C—Si stretching mode of H₂C—SiH₂ has been observed with a frequency 985 cm^{-1} .²³ The calculated results shown in Table II indicate that the C—Si stretching frequency of 1 should be ca. 60 cm^{-1} lower than that of silaethylene. A frequency shift toward higher wave numbers by ca. 130 cm^{-1} is predicted for the C—Si stretching mode of 2 relative to 1. A previous theoretical study of 2 gave an estimated value of 1092 cm^{-1} based on CISD/DZP calculations,⁵ which is in reasonable agreement with the frequency predicted here (1059 cm^{-1}). The very high-lying isomer 3 is calculated with a significantly lower C—Si frequency (804 cm^{-1}). The C—Si stretching modes of 1 and 2 have a rather low IR intensity (Table II). The Si—H stretching frequency of 2 predicted at 2260 cm^{-1} could be more helpful to identify silaacetylene. The three CSiH₂ isomers should also be clearly distinguished by microwave spectroscopy. The calculated rotational constants of 1, 2, and 3 show that the large A value is quite different for the three isomers (Table II). Also, the dipole moments of the three isomers are very different from each other.

To investigate the carbon-silicon bonding situa-

TABLE II.
Calculated Harmonic Vibrational Frequencies (cm^{-1}), Dipole Moments (Debye), Infrared Intensities (km mol^{-1}), and Rotational Constants (MHz) at CCSD(T) / TZ2P.

No.	Frequencies	Description	IR Intensities	Rotational Constants	Dipole Moment	
1	330.9	CH ₂ wag (b ₁)	0.83	A	303027	0.17
	682.8	CH ₂ rock (b ₂)	106.72	B	16249	
	925.3	C—Si stretch (a ₁)	8.96	C	15423	
	1360.6	CH ₂ scissors (a ₁)	18.44			
	3096.1	Symmetric C—H stretch (a ₁)	0.04			
	3176.6	Asymmetric C—H stretch (b ₁)	1.45			
2	472.7	C—Si—H bend (a')	33.48	A	332485	0.87
	596.0	Out-of-plane (a'')	68.36	B	16999	
	733.6	Si—C—H bend (a')	61.51	C	16172	
	1059.4	C—Si stretch (a')	4.77			
	2260.6	Si—H stretch (a')	17.14			
	3273.7	C—H stretch (a')	0.83			
3	286.1	SiH ₂ rock (b ₂)	0.43	A	157279	2.54
	295.8	SiH ₂ wag (b ₁)	63.97	B	16662	
	804.5	C—Si stretch (a ₁)	66.74	C	15066	
	936.2	SiH ₂ scissors (a ₁)	4.66			
	2258.9	Symmetric Si—H stretch (a ₁)	13.65			
	2295.8	Asymmetric Si—H stretch (b ₁)	44.37			

tion in the CSiH_2 isomers, we analyzed the wave function using the NBO method.¹¹ This part of the study was carried at the MP2/TZ2P level of theory, because the current programs for analyzing the electronic structure cannot handle CCSD(T) wave functions and densities. The results of the NBO analysis are shown in Table III.

The NBO analysis suggests that in all CSiH_2 isomers the carbon atom carries a large negative partial charge, in particular in **1** and **2**, while the silicon atom has a significant positive partial charge. As expected, the hydrogen atoms bonded to carbon are positively charged while the silicon-bonded hydrogen atoms are negatively charged. Two C—Si bonds are calculated for **1** by the NBO scheme, a σ and a π bond (Table III). Both C—Si bonds are significantly polarized toward the carbon end, as shown by the %Si value. This is why the carbon atom of **1** carries a large negative charge of -1.30 . The NBO scheme thus indicates that the carbon-silicon bond of **1** has a substantial ionic contribution. We calculated also the NLMO (natural localized molecular orbital)²⁴ bond order BO, which is based on the shared occupancies and hybrid overlaps of the NAOs (natural atomic orbitals)²⁵ composing the NLMO.²⁶ The advantage of this method is that it gives individual bond orders for each bond orbital. Table III shows that the bond order of the C—Si σ bond is lower (0.48) than calculated for the π bond (0.64). This is because the latter bond is less polarized than the σ bond. The sum of the bond order contributions to the C—Si bond (which includes small contributions by other bond orbitals) is only 1.15.

The NBO scheme calculates three C—Si bonds for bent silaacetylene (**2**) (Table III). This result should not be overinterpreted. The C—Si bond length of **2** calculated at MP2/TZ2P is rather short (1.628 Å, Fig. 1). The C—Si σ bond is strongly polarized toward the carbon end, which is nearly sp hybridized. The C—Si π bond of **2** is also clearly polarized toward C, while the third C—Si bond shows a small polarization toward the silicon end. This bond has practically only p character at the carbon atom. Because of the nearly equal contribution of the carbon and the silicon atom, the third bond has a high bond order 0.92. The total bond order for the C—Si bond of silaacetylene (**2**) is 2.10, which is significantly higher than the bond order of **1**. The C—Si bond order of the linear form **4** is 2.27 (Table III). The energetically high-lying isomer **3** has an intermediate bond order 1.69. The C—Si bond order of **3** is higher than the bond order of **1** (1.15), although **1** has a shorter C—Si bond than **3** (Fig. 1). The NBO analysis calculates σ and π contributions to the C—Si bond which are much less polarized in **3** than in **1**. It follows that the shorter C—Si bond of **1** is due to the significantly larger charge attraction (see the partial charges in Table III). The C—Si bond of **1** is much more ionic than the C—Si bond of **3**.

SUMMARY AND CONCLUSION

There are three local energy minimum structures on the CSiH_2 potential energy surface in the singlet electronic ground state. The global mini-

TABLE III.
Results of the NBO Analysis at MP2 / TZ2P.^a

No.	$q(\text{C})$	$q(\text{Si})$	$q(\text{H})$	C—Si					BO	ΣBO
				%Si	%s(Si)	%p(Si)	%s(C)	%p(C)		
1	-1.30	0.84	0.23	23.9	20.5	78.8	39.3	60.0	0.48	1.15
				31.8	0.0	99.0	0.0	99.8	0.64	
2	-0.95	0.90	0.20 (C)	25.8	21.9	77.4	56.5	43.2	0.52	2.10
			-0.15 (Si)	32.8	0.0	99.7	0.0	99.6	0.65	
				53.7	36.1	63.8	1.7	98.0	0.92	
3	-0.33	0.62	-0.15	39.2	37.4	62.1	24.1	75.0	0.80	1.69
				43.5	0.0	99.2	0.0	99.6	0.87	
4	-0.89	0.78	0.20 (C)	32.5	53.3	46.9	52.7	47.1	0.65	2.27
			-0.08 (Si)	40.4	0.0	99.6	0.0	99.9	0.81	
				40.4	0.0	99.6	0.0	99.9	0.81	

^aPartial atomic charges q and analysis of the C—Si bond. Polarity given by %Si, hybridization of C and Si, bond order BO.

mum is the silylidene form **1**, which has a carbon-silicon double bond with a bond length 1.721 Å at CCSD(T)/TZ2P. The trans-bent silaacetylene isomer **2** is 34.1 kcal mol⁻¹ higher in energy than **1** at CCSD(T)/TZ2P(fd) + ZPE. The barrier for rearrangement **2** → **1** is predicted at the same theoretical level to be 5.1 kcal mol⁻¹. Silaacetylene **2** has a calculated bond length C—Si = 1.665 Å at CCSD(T)/TZ2P, which is in the middle between the carbon-silicon double bond of **1** and the triple bond of the linear form HCSiH (**4**) [C—Si (**4**) = 1.604 Å]. Structure **4** is a higher-order saddle point (*i* = 2) on the potential energy surface. The third local minima is the energetically very high-lying vinylidene isomer **3**. Structure **3** is 84.1 kcal mol⁻¹ less stable than **1** [CCSD(T)/(fd) + ZPE]. The barrier for isomerization **3** → **2** is only 2.7 kcal mol⁻¹ at CCSD(T)/TZ2P(fd) + ZPE. The NBO analysis indicates substantial ionic contributions to the carbon-silicon bonds of **1** and **2**.

The carbon-silicon bonds of the CSiH₂ isomers are polarized toward the carbon end. In particular, the global energy minimum silylidene (**1**) has a negatively charged carbon atom, and the C—Si bond has a significant ionic character. The carbon-silicon bond of trans-bent silaacetylene (**2**) should be considered as intermediate between a double and a triple bond.

It will be very difficult to observe **3** experimentally, but the identification of the silaacetylene isomer (**2**) might be possible. The theoretically predicted harmonic vibrational frequencies, IR intensities, rotational constants, and dipole moments should be helpful for experimental studies.

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